



Oxidation and reduction of mercury by SCR DeNOx catalysts under flue gas conditions in coal fired power plants



Raik Stolle^a, Heinz Koeser^{a,*}, Heinz Gutberlet^b

^a Centre of Engineering Science, Chair of Environmental Technology, Martin-Luther-University Halle-Wittenberg, D-06099 Halle, Saale, Germany

^b D-46348 Raesfeld, Germany

ARTICLE INFO

Article history:

Received 27 March 2013

Received in revised form 13 July 2013

Accepted 16 July 2013

Available online 24 July 2013

Keywords:

Mercury emission control

Mercury oxidation

Mercury reduction

Induced reduction

SCR DeNOx catalyst

ABSTRACT

The co-oxidation of elemental mercury (Hg) in SCR DeNOx reactors to water soluble oxidised species followed by co-removal in flue gas desulphurisation scrubbers is a promising way to reduce these emissions from fossil fuel fired power plants.

This paper looks at the results of a series of lab experiments on the oxidation and reduction of Hg by commercial $V_2O_5/WO_3(MoO_3)/TiO_2$ honeycomb and plate type DeNOx catalysts.

It could be shown that at a given hydrogen halide content the oxidation of elemental Hg on DeNOx inactive material follows a first order reaction with respect to the Hg concentration. On the basis of mass concentration, HBr was ten times more effective than HCl in promoting the oxidation of elemental Hg under otherwise identical conditions. The oxidation of elemental Hg increased with increasing vanadium content in the catalysts. The Hg oxidation activities of several commercial SCR catalysts were determined for the DeNOx inactive case and compared with their DeNOx activities. In this way, it was possible to show that the velocities of Hg oxidation and DeNOx reaction are of the same order of magnitude.

The DeNOx-active state of the catalysts had a strongly negative impact on the oxidation of elemental Hg that could not be explained solely by an inhibition effect of ammonia. Under these conditions, even reduction of oxidised Hg occurred on the catalyst. The same reduction occurred for SCR DeNOx catalysts when oxidising volatile organic hydrocarbons. This effect was called induced mercury reduction. The observed oxidation rate of Hg on DeNOx- and VOC-active catalysts is the net sum of an oxidation and a reduction reaction which take place in parallel. Our understanding of the control variables for Hg oxidation in SCR DeNOx plants has to be amended in light of these slowing effects and has to take the induced reduction into account.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Mercury (Hg) is regarded as a hazardous air pollutant [1]. In addition to natural sources such as volcanoes, anthropogenic combustion sources are also major emitters of Hg into the atmosphere. Once emitted, in particular elemental mercury (Hg^{el}) is transported long distances before being deposited into water and sediments, so it is a global environmental pollutant. In aquatic ecosystems, Hg may be transformed into highly toxic methyl-Hg, which bio-accumulates in living organisms and bio-magnifies in higher trophic levels. Human beings are affected when they consume methyl-Hg-contaminated fish. For these reasons, the United Nations Environment Programme (UNEP) and several governments and private institutions have recently initiated several studies on

Hg in order to control its emission into the atmosphere. Up-to-date studies on Hg emissions and proven removal options which are available are important for the development of a global consensus on the control of Hg emissions [2].

Oxidised mercury (Hg^{ox}) is fairly water soluble and therefore amenable to co-removal in flue gas desulphurisation (FGD) scrubbers. Elemental mercury (Hg^{el}) cannot be removed because of its low solubility [3]. Adsorbents such as activated carbon are required for capture in this case. For mercury emission control in flue gases, it is preferable to have the mercury as an Hg^{ox} species upstream of the wet FGD.

Mercury enters coal-fired power plants with the fuel. Due to the high incineration temperature, almost all of the mercury introduced is transformed into the volatile elemental form. The Hg^{el} leaving the furnace in the flue gases is subsequently oxidised in a number of complex reactions when the temperature decreases in the boiler [4,5]. The gas phase oxidation is kinetically restrained, so that elemental and oxidised mercury are both found in the flue gas leaving the boiler. The ratio of elemental to oxidised mercury

* Corresponding author. Tel.: +49 3461 46 2542; fax: +49 3461 46 2710.

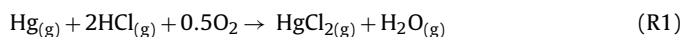
E-mail addresses: r.stolle@gmx.de (R. Stolle), heinz.koeser@iw.uni-halle.de (H. Koeser), hgutberlet@t-online.de (H. Gutberlet).

varies depending on the exhaust gas composition and the flue gas cooling process.

DeNOx catalysts generally consist of titanium dioxide (TiO₂), the catalytically active component vanadium pentoxide (V₂O₅) and tungsten trioxide (WO₃) and/or molybdenum trioxide (MoO₃) as activators [6]. Due to the oxidation potential of the vanadium pentoxide various side reactions may run in parallel in addition to the DeNOx reaction, such as the oxidation of organic hydrocarbons, the conversion of SO₂ into SO₃ or the formation of oxidised mercury [7,8].

In the nineties, investigations were already able to show that SCR DeNOx plants maintain in addition to NO reduction Hg oxidation [9]. Hg oxidation of 90% and above is recorded provided that the flue gas contains abundant Cl species and that the SCR reactor has sufficient activity and residence time. When these conditions are met, the combination of SCR, electrostatic precipitator and wet FGD controls the Hg emission without requiring additional chemicals or equipment [3]. More recent research programmes and measurement campaigns in power stations have made it clear that a number of factors influence the oxidation of mercury by SCR DeNOx catalysts [10,11].

The halogen content in the flue gas is considered to be one of the most important parameters. Since HCl is the dominant halide species in flue gases, Hg^{el} oxidation on SCR DeNOx catalysts is thought to occur in accordance with the following overall equation:

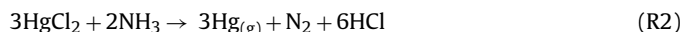


In the absence of halogen species in the flue gas to be treated, Hg is absorbed by DeNOx catalysts [12]. There is also sufficient evidence for adsorption of HCl on the surface of the catalyst [11,13]. The adsorption of HCl will lead to activated if not oxidised chlorine species. It is not clear yet whether the adsorbed and oxidised HCl is reacting with gaseous Hg or adsorbed and oxidised Hg is reacting with gaseous HCl to be released into the gas phase as

HgCl₂. The reaction of adsorbed Hg with adsorbed HCl according to a Langmuir–Hinshelwood mechanism followed by desorption of HgCl₂ from the catalyst surface is also mentioned in literature as a third possible reaction pathway [11].

A large number of studies mention the negative effect of NH₃ addition on Hg^{el} oxidation by SCR catalysts in the presence of HCl and NOx [14–16]. This may be explained by a competitive adsorption of NH₃ with Hg. Other authors see the underlying course as the competition between NH₃ and HCl [17,18]. Because of this negative effect of NH₃, mercury oxidation takes place more towards the outlet of SCR catalyst layer after the NH₃ is consumed by the DeNOx reaction.

Recently it was pointed out that at temperatures greater 325 °C ammonia may also reduce oxidised mercury [19] in accordance with the following reaction:



The Hg oxidation observed reflects the net sum of the oxidation (R1) and the reduction (R2) reaction.

This paper describes the methodology, results and conclusion of a lab-scale investigation into mercury oxidation and reduction on SCR catalysts. The flow and temperature conditions and the model gas composition were adjusted to the conditions of a high-dust SCR DeNOx plant in hard-coal fired power plants. Commercial honeycomb and plate type material catalysts have also been investigated.

The aim was to gain a deeper understanding of the reaction involving mercury oxidation across DeNOx catalysts. One focus was on the reduction reactions of mercury on these catalysts that have mostly been neglected thus far. The results of the study should lead to a more effective control of Hg oxidation in DeNOx plants.

2. Experimental

The focus of the present investigation was the simulation of mercury co-oxidation occurring in industrial DeNOx plants. The

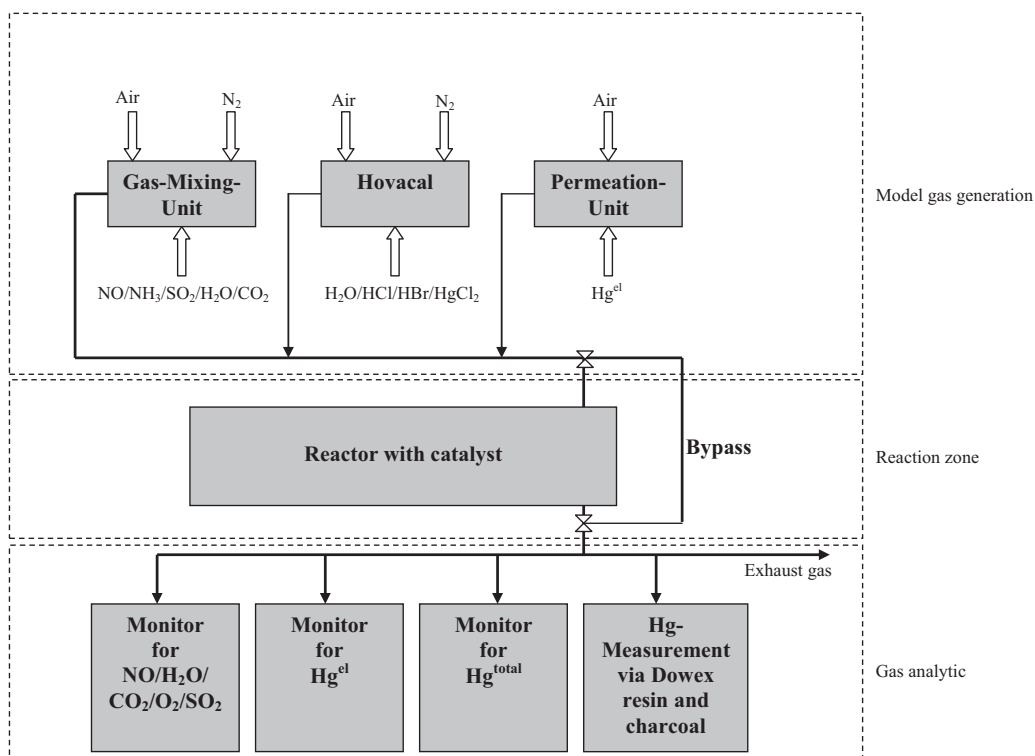


Fig. 1. Schematic view of the micro-bench test flow reactor.

Table 1
Chemical and physical properties of the SCR-DeNOx-catalysts.

| Catalyst | V ₂ O ₅ content (wt.%) | WO ₃ content (wt.%) | MoO ₃ content (wt.%) | Pitch (mm) | Channel (mm) | Specific geometric surface area (m ² /m ³) | Comment |
|----------|--|--------------------------------|---------------------------------|------------|--------------|---|--|
| H1 | 0.60 | 10.0 | 0.03 | 7.33 | 6.07 | 427 | New material |
| H2 | 0.60 | 10.0 | 0.03 | 7.33 | 6.07 | 427 | Identical with H1 but used material |
| H3 | 0.72 | 8.5 | <0.03 | 6.05 | 5.25 | 500 | New material |
| H4 | 0.71 | 9.3 | 0.03 | 6.05 | 5.15 | 490 | New material |
| H5 | 0.74 | 8.9 | 0.04 | 7.16 | 6.34 | 440 | New material |
| H6 | 0.28 | 5.4 | 0.03 | 7.11 | 6.08 | 420 | New material |
| H7 | 2.60 | 9.6 | 0.04 | 4.20 | 3.50 | 760 | New material |
| H8 | 0.00 | 9.6 | 0.04 | 4.20 | 3.50 | 760 | Identical with H7 but without vanadium |
| H9 | 0.72 | 9.6 | – | 9.20 | 8.45 | 383 | New material |
| P1 | 1.02 | 0.27 | 3.1 | 4.00 | 3.00 | ~500 | New material |
| P2 | 1.14 | 19.5 | – | 4.00 | 3.00 | ~500 | New material |
| P3 | 1.52 | 12.0 | – | 4.00 | 3.00 | ~500 | New material |

experiments were designed for this purpose. Consequently the catalysts studied were shaped as monolith ore plates. In order to develop more fundamental pieces of evidence the use of powdered catalysts would have been preferable to reduce the effect of the external mass transfer.

2.1. Flow reactor

The laboratory test reactor (see Fig. 1) used for the investigations consists of the units: gas generation, reactor and gas analysis. A detailed description of the experimental set-up was given in [12]. The catalyst samples were cut from technical honeycomb catalysts with 2 × 2 or 4 × 4 channels and lengths of 0.05–0.35 m. Plate catalysts were placed in a special holder for between two and four plates with a length of 0.25 m and a width of 16 mm. The catalyst samples were placed in a glass reactor consisting of two concentric tubes as described in [12]. The temperatures upstream and downstream of the catalyst were measured under test condition before the experiments.

The investigations were performed under standard conditions with the DeNOx reactor at 390 °C, an oxygen concentration in the model flue gas of 4% by volume (dry), a moisture content of 7% by volume and 100 mg/m³ HCl.

2.2. Mercury adsorption

The investigation was conducted at 390 °C with 0.5 g of the catalysts as fragments embedded in rock wool in the reaction chamber of the flow reactor, see [12] for details.

2.3. Mercury analysis

In order to measure the total and elemental mercury concentrations at the inlet and the outlet of the reactor, two mercury emission monitors (HM 1400, Model EPM 791.907, Durag, Verewa, Germany) with wet chemistry for flue gas preparation were used [12]. The remaining SO₂ in the scrubbed and dried sample gas was removed by an adsorber filled with NaOH granules. By evaporating a defined HgCl₂ solution with the Hovacal system (IAS/Germany) in a known gas stream the Hg analysers were regularly calibrated with a gas containing a total mercury concentration of 100 µg/m³.

From time to time, sorbent-trap measurements were made in parallel to the continuous mercury monitors. In the sorbent traps, a layer with Dowex™ 1 × 8 fine mesh resin for the oxidised Hg was followed by a layer of iodised activated carbon pellets for the remaining elemental Hg [20]. The mercury content on the absorber layers was analysed using a pyrolytic method.

The HM 1400 mercury monitor had a detection level of around 2 µg/m³. In order to have steady mercury signals it was important

to keep the heating tubes that delivered the sample gas to the scrubbing units of the mercury monitors at a temperature of at least 180 °C to avoid deposition of oxidised mercury.

Determining the elemental mercury in the model gases with added HBr proved to be difficult. Here, sodium chloride ore sodium thiosulfate had to be added to the HCl scrubbing solution used for removing the oxidised mercury. After introducing this modification to the scrubber, a reasonable correlation between the results of the elemental mercury monitor and the Dowex/active carbon sorbent-trap method was achieved.

Stationary conditions of the mercury concentration downstream of the catalyst, as measured by the mercury monitor, were achieved 1–4 h after changing the conditions in most experiments.

2.4. Gas analysis for non-mercury pollutants

The gas components H₂O, SO₂, NO and O₂ were continuously measured using a multi component BINOS analysis system from Emerson Process equipped with a hot (200 °C) photometric cell (formerly Leybold-Heraeus GmbH). A paramagnetic OXYNOS analyser was used to measure the concentration. All of these devices were regularly calibrated with conventional certified reference gases.

2.5. Chemicals and gases

See remarks in [12].

2.6. Catalysts

Characteristic parameters of the catalysts investigated are summarised in Table 1. The catalysts samples were conditioned for 48 h at 390 °C with the model gas with 2000 mg/m³ of SO₂ and for a further 48 h with 400 ppm NO and 200 ppm NH₃ added.

The length of the sample catalysts and the flue gas flow were adjusted to simulate flow conditions and residence times characteristic for one, two and three catalyst layers of a commercial SCR DeNOx plant. For this, area velocities (AV = ratio of flue gas volume under standard conditions per geometric surface area of catalyst) of 19.7 m/h, 11.6 m/h and 5.8 m/h were selected.

3. Results and discussion

3.1. Mercury adsorption on SCR DeNOx catalysts

The mercury adsorption capacities of the catalyst listed in Table 1 were determined at 390 °C and at an Hg concentration of 40 µg/m³.

In the halogen-free model gas, the following mercury equilibrium loadings were measured:

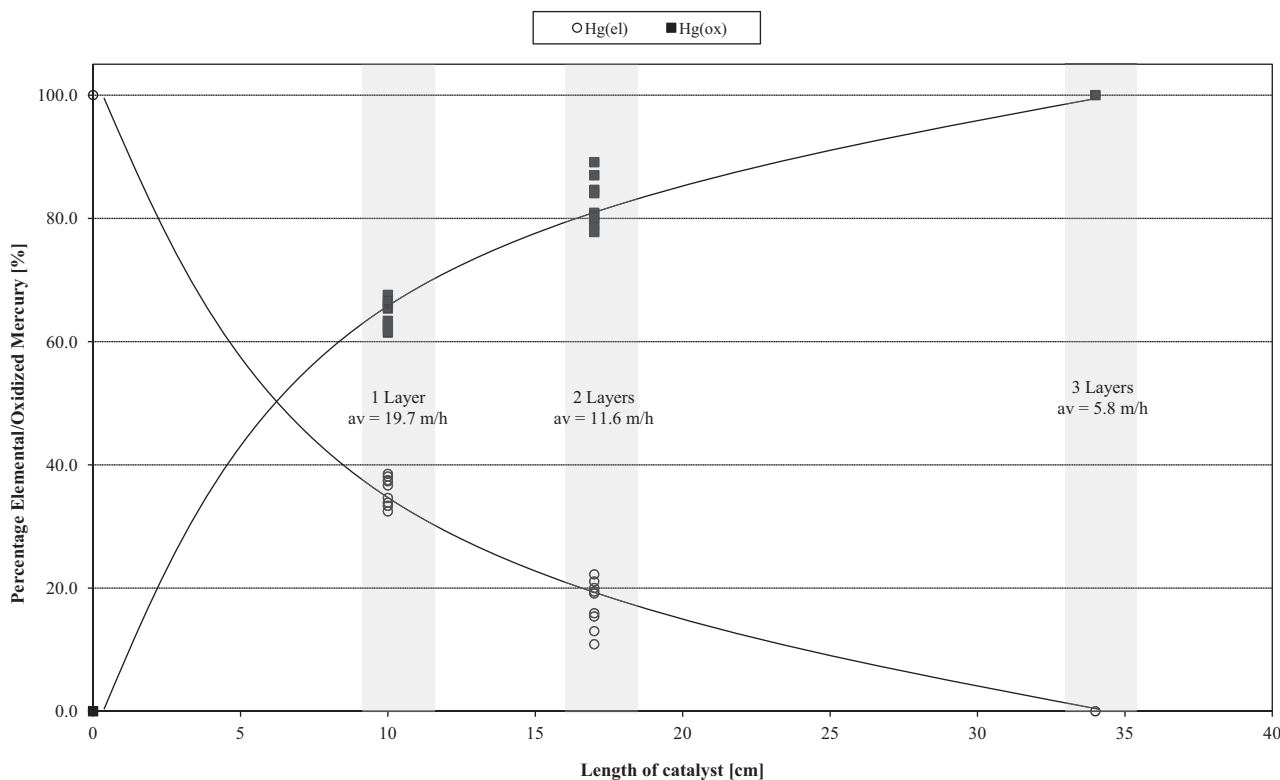


Fig. 2. Percentage of elemental mercury as function of the length of the SCR catalyst at a constant model flue gas flow (influent model gas flow with 10–100 $\mu\text{g}/\text{m}^3$ elemental mercury, 100 mg/m^3 HCl, 4% by volume (dry) O_2 , 7% by volume H_2O , no NO, NH_3 and SO_2 , 390 °C).

- elemental Hg: 2.1–3.9 mg/kg
- oxidised Hg (as HgCl_2): 14–82.5 mg/kg

The results show that even at 390 °C DeNOx catalysts are capable of adsorbing fairly high levels of Hg. The Hg-loading increased with increasing vanadium content in the catalysts. The oxidised Hg was more strongly adsorbed than the elemental by a factor of two.

When increasing the hydrogen halide concentration in the flue gas model. It was possible to show that concentrations of $\sim 5.0 \text{ mg}/\text{m}^3$ HCl or $\sim 0.5 \text{ mg}/\text{m}^3$ HBr suppressed the adsorption of Hg below the limit which can be detected. Given these small effective concentrations of halogen halides, the Hg loading of high dust SCR DeNOx catalysts in coal fired power plants should be negligible. These findings confirm results reported in the literature [12,15].

3.2. Mercury oxidation and reduction by DeNOx-inactive SCR catalysts

In the course of the investigation it became apparent that the mercury oxidation activity of SCR DeNOx catalyst in the presence of NO and NH_3 in the influent gas, the “DeNOx-active status” of the catalyst differs considerably from a DeNOx-inactive catalyst, (without the presence of NH_3 and NO in the influent gas at the same time). This chapter will discuss the results of investigations on the DeNOx-inactive catalyst.

3.2.1. Reaction order of Hg oxidation on SCR catalysts

In Fig. 2, the oxidation of Hg^{el} on the H1 honeycomb catalyst is shown as a function of the length and area velocity (AV) respectively (for the standard model flue gas at 390 °C). The influent gas contained exclusively elemental Hg. Under the chosen conditions for an area velocity of 19.7 m/h nearly 65.0% of the elemental mercury was oxidised, whereas at 5.8 m/h the elemental mercury was

almost fully oxidised. Decreasing AV resulted in an increasing percentage of oxidised mercury downstream of the catalyst.

The detailed investigation showed that for a given gas composition, catalyst, temperature and area velocity (AV) the degree of Hg oxidation was not linked to the concentration of the elemental mercury (in the range from 10 to 100 $\mu\text{g}/\text{m}^3$) in the influent gas. All of the investigations resulted in a comparable oxidation ratio at a given AV. When varying the AV, the oxidation could be described as a reaction of the order of 1 in the Hg^{el} concentration within the uncertainty of the measurement. Consequently, the Hg^{el} oxidation potential was expressed by the Hg oxidation activity f_{Hg} according to equation (Eq. (1)), in a similar manner to the DeNOx activity of the SCR catalyst [21]:

$$f_{\text{Hg}} = -AV \times \ln \left(1 - \frac{c_{\text{Hg}^{\text{el}}}^{\text{in}} - c_{\text{Hg}^{\text{el}}}^{\text{out}}}{c_{\text{Hg}^{\text{el}}}^{\text{in}}} \right) \quad [\text{m}/\text{h}] \quad (1)$$

f_{Hg} is the mercury oxidation activity in a given flue gas (m/h); AV is the area velocity (m/h); $c_{\text{Hg}^{\text{el}}}^{\text{in}}$ is the inlet elemental mercury concentration ($\mu\text{g}/\text{m}^3$); $c_{\text{Hg}^{\text{el}}}^{\text{out}}$ is the Outlet elemental mercury concentration ($\mu\text{g}/\text{m}^3$).

3.2.2. Comparison of Hg oxidation and DeNOx activity of commercial SCR catalysts

In Fig. 3, the mercury oxidation activities measured (as defined in Eq. (1)) for the catalysts from Table 1 are presented as a function of the vanadium pentoxide content of the respective catalyst. The activity data were determined in the model flue gas (with the model gas 40 $\mu\text{g}/\text{m}^3$ elemental mercury, 4% by volume O_2 , 7% by volume H_2O and 100 mg/m^3 HCl) at 390 °C. The catalysts cover a wide range of activities from 8 to 86 m/h . Hg oxidation activity is increasing with increasing V_2O_5 concentration in the SCR catalyst. The highest mercury oxidation activity of 86.6 m/h was measured

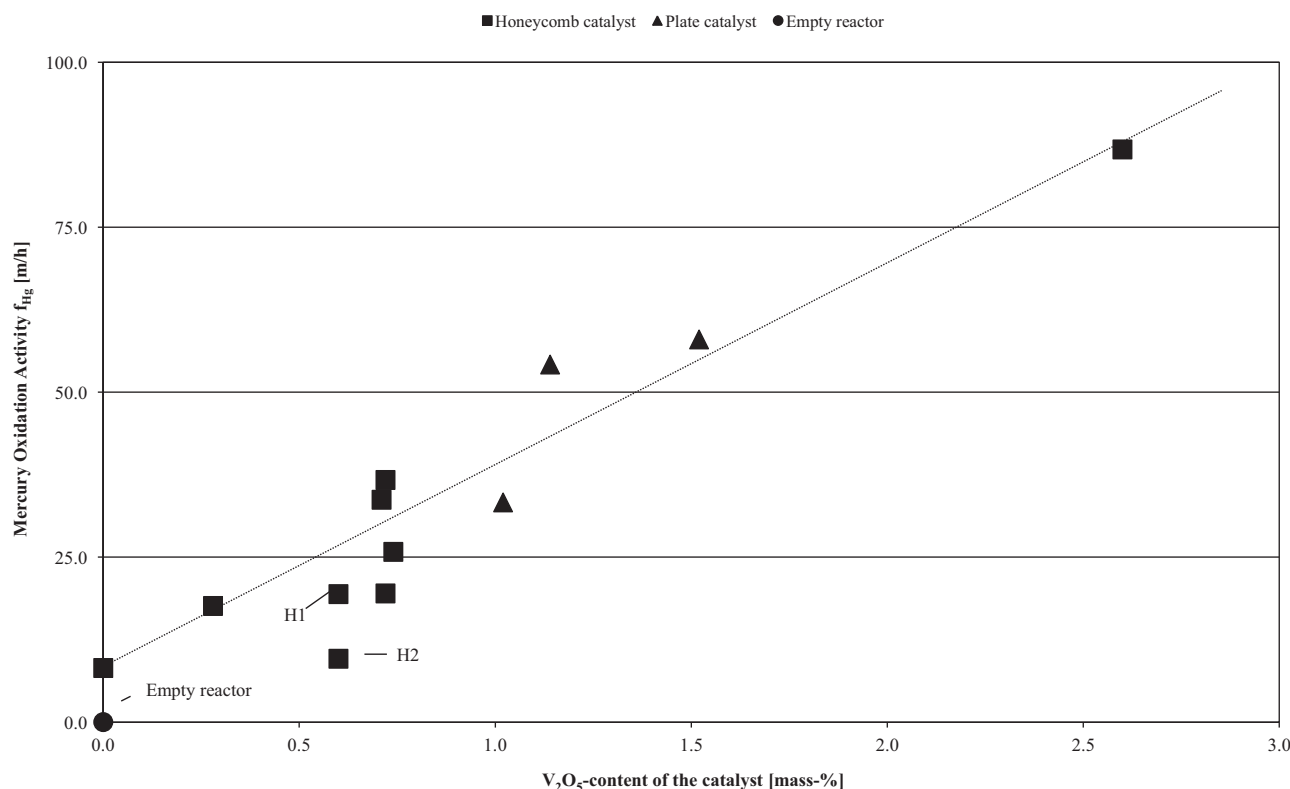


Fig. 3. Mercury oxidation activity f_{Hg} of commercial SCR DeNOx catalysts as function of their V content (influent model flue gases with $40 \mu\text{g}/\text{m}^3$ elemental mercury, $100 \text{ mg}/\text{m}^3$ HCl, 4% by volume (dry) O_2 , 7% by volume H_2O and no NO, NH_3 and SO_2 , 390°C).

for the H7 catalyst with 2.6% by weight V_2O_5 . This catalyst is used as a tail-end catalyst. The lowest oxidation factor of 8.2 m/h was measured for the almost vanadium-free test catalyst H8. Here, the Hg^{el} oxidation is caused by the WO_3 and the TiO_2 support. By comparing the catalysts samples H1 and the H2 (identical catalysts but with H2 having already been used and aged for 100,000 operating hours in an SCR DeNOx plant showing CaSO_4 blinding), the effect of ageing and deactivation is seen. The activity of the catalyst in the DeNOx plant caused a decrease in mercury oxidation activity from 20.5 m/h for the new catalyst to 9.6 m/h for the aged material H2. The DeNOx activity was lowered to the same degree as seen in Table 2.

Table 2 lists the Hg oxidation activities and the corresponding DeNOx activities of the catalysts investigated under comparable conditions. The values of the Hg and DeNOx activities of a catalyst are of the same order of magnitude. The DeNOx activity may be twice as high as the Hg activity. However, in two cases the Hg activity is slightly higher. Obviously, Hg oxidation of a SCR catalyst is a

fairly rapid reaction compared to the DeNOx reaction, and much faster than SO_2 conversion. Consequently, Hg oxidation will take place in the outer layer of the porous catalyst in a similar manner to the DeNOx reaction.

It has to be noted that Hg oxidation activity increased when the operating temperature was lowered from 390 to 360°C (data not shown). This anomalous temperature effect has been observed also by other investigators, see also [19].

3.2.3. Effect of HCl and HBr on Hg oxidation of DeNOx-inactive SCR catalysts

In Fig. 4, the effect of the HCl concentration (10 and $100 \text{ mg}/\text{m}^3$) on the oxidation of elemental mercury by four commercial catalysts at 390°C is given. An increase in the HCl concentration led to higher oxidation activity for mercury. The highest sensitivity of the mercury oxidation activity to the HCl concentration was from 5 to $40 \text{ mg}/\text{m}^3$. The different absolute values of the oxidation activity in the catalysts investigated were partly due to their vanadium content, see Fig. 3. From Fig. 4 it can be seen that HCl in the gas phase may compensate for a lack of inherent Hg oxidation potential in the catalyst to a certain degree. In coal fired power plants, the HCl in the flue gas is determined by the chlorine content of the incinerated coal. In this respect it is also of interest that in recent pilot plant investigations the NH_3 required for the DeNOx process was substituted partially by NH_4Cl in order to increase the HCl [22]. The data in Fig. 4 suggest that this addition should be especially effective in cases where the coal derived HCl content of the flue gas is below $40 \text{ mg}/\text{m}^3$.

Coals contain also bromine. The bromine content is generally between 1% and 5% of its chlorine content [23]. Some power plants add bromide to the boiler to increase the mercury oxidation in the gas phase [24]. In the incineration and subsequent cooling process, the fuel bromine or added bromide is eventually transformed into HBr. The effect of HBr on the oxidation of elemental mercury in

Table 2

Comparison of mercury oxidation (k_{Hg} , DeNOx-inactive) and DeNOx activities (k_{DeNOx}) of commercial honeycomb and plate SCR DeNOx catalysts.

| Catalyst | k_{DeNOx} (m/h) | k_{Hg} (m/h) | k_{DeNOx}/k_{Hg} (l) |
|----------|--------------------------|----------------|-------------------------------|
| H1 | 38.4 | 20.5 | 1.9 |
| H2 | 17.7 | 9.6 | 1.8 |
| H3 | 54.1 | 36.4 | 1.5 |
| H4 | 48.4 | 33.4 | 1.4 |
| H5 | 38.5 | 25.8 | 1.5 |
| H6 | 39.1 | 19.5 | 2.0 |
| H7 | 36.5 | 17.6 | 2.1 |
| H8 | 69.2 | 86.6 | 0.8 |
| H9 | 15.6 | 8.2 | 1.9 |
| P1 | 56.1 | 33.3 | 1.7 |
| P2 | 65.8 | 54.2 | 1.2 |
| P3 | 55.6 | 58.0 | 1.0 |

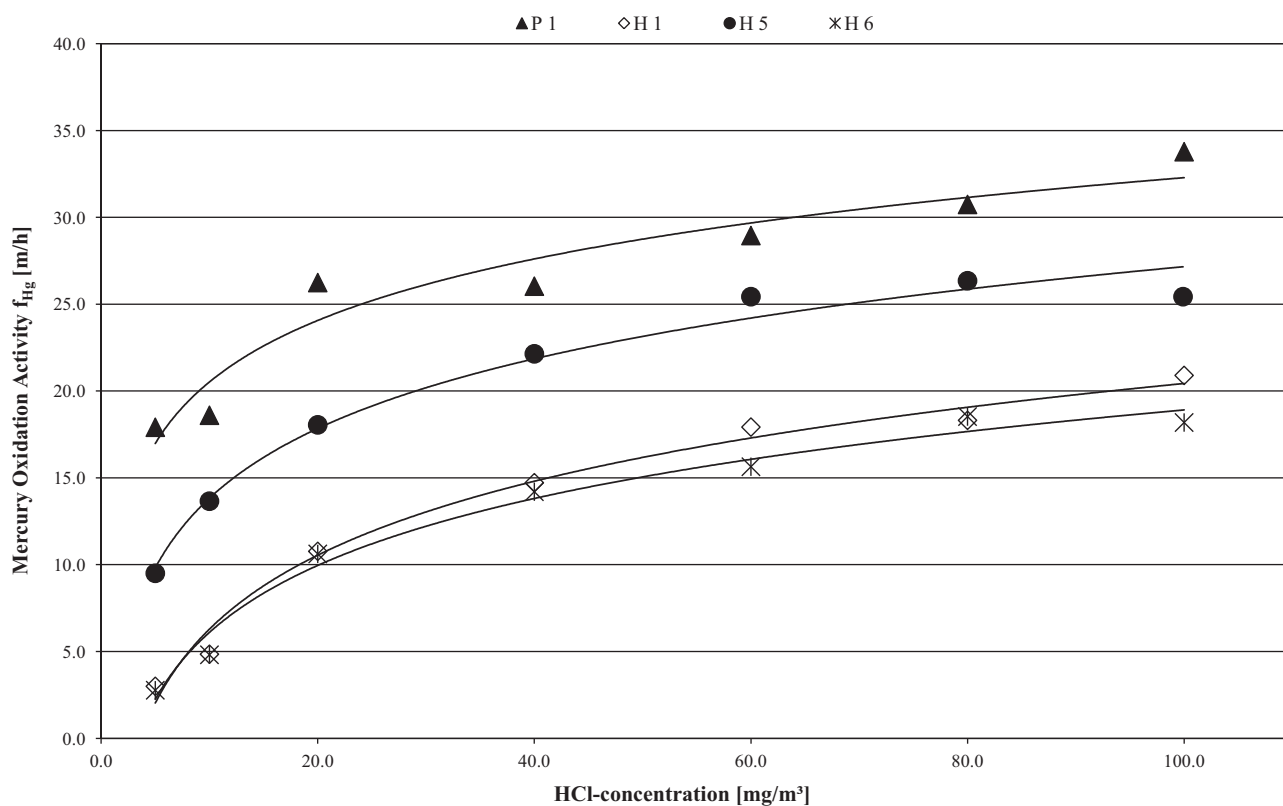


Fig. 4. Mercury oxidation activity f_{Hg} of the SCR DeNOx H1 catalyst as function of the HCl concentration in the gas (influent model flue gas with $40 \mu\text{g}/\text{m}^3$ elemental mercury, 4% by volume (dry) O_2 , 7% by volume H_2O and no NO , NH_3 and SO_2 , 390°C).

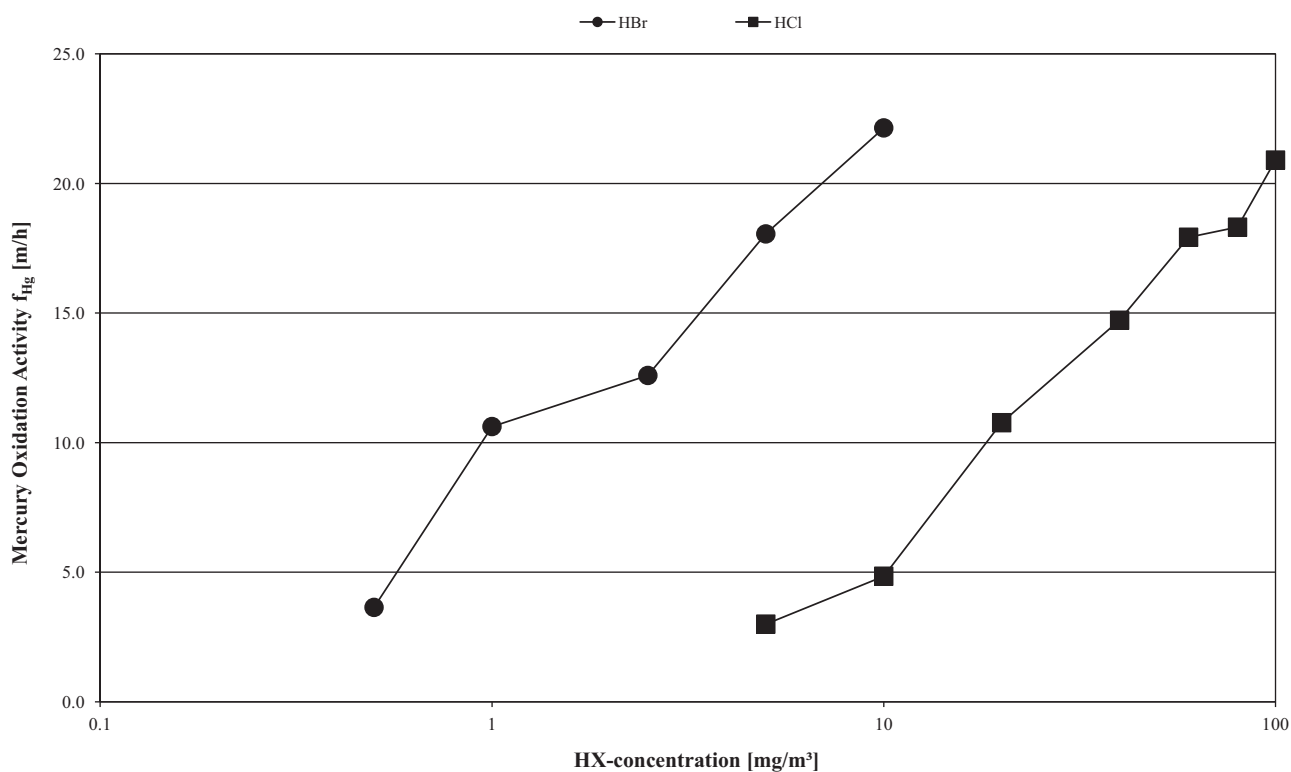


Fig. 5. Comparison of the effects of the HBr and HCl concentration in the gas on the mercury oxidation activity f_{Hg} of the SCR-DeNOx H1 catalyst (influent model flue gas with $40 \mu\text{g}/\text{m}^3$ elemental mercury, 4% by volume (dry) O_2 , 7% by volume H_2O and no NO , NH_3 and SO_2 , 390°C).

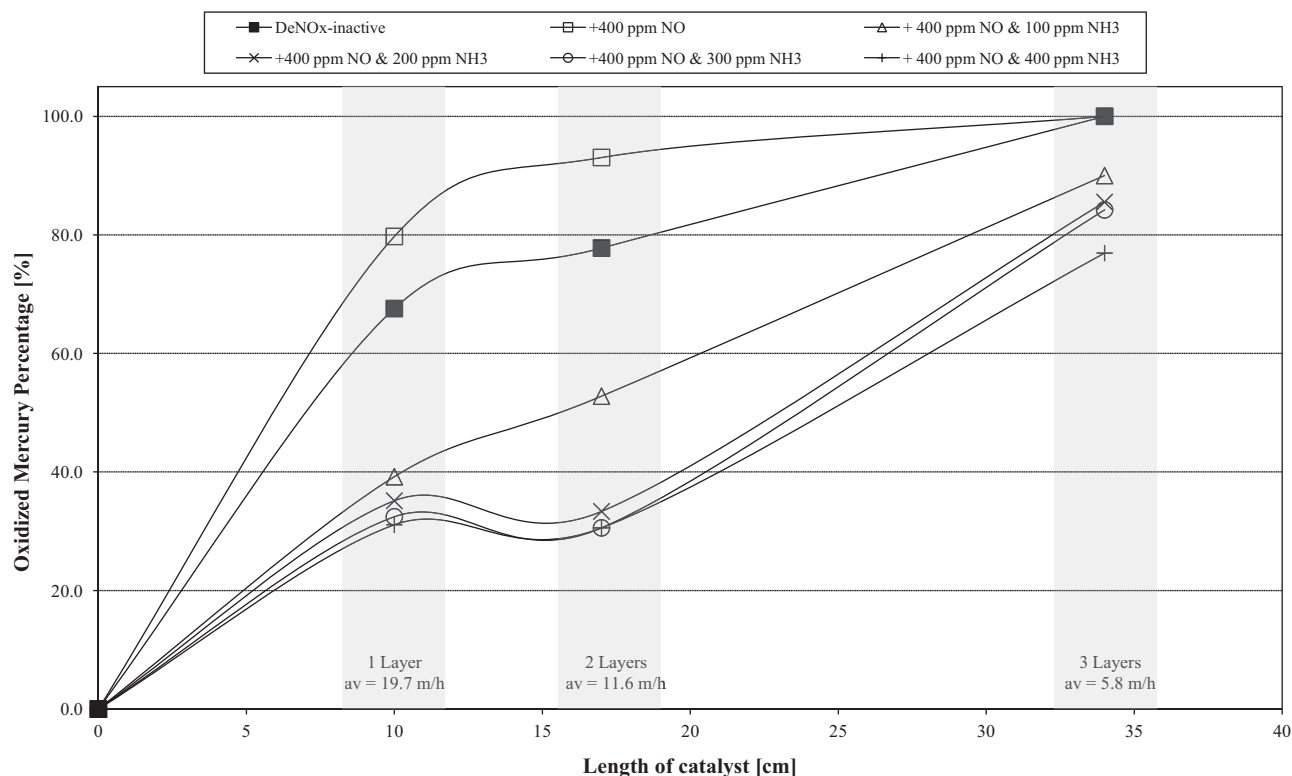


Fig. 6. Percentage of oxidised mercury downstream of DeNOx-inactive (no NH_3 and NO) and DeNOx-active (with different NH_3/NO ratio) H1 catalyst as function of catalyst length/area velocity AV (influent model flue gases flow with $40 \mu\text{g}/\text{m}^3$ elemental mercury, $100 \text{ mg}/\text{m}^3$ HCl, 4% by volume (dry) O_2 , 7% by volume H_2O , 390°C).

the presence of the honeycomb catalyst H1 in comparison to HCl is given in Fig. 5. It should be noted that the hydrogen halide concentration axis in Fig. 5 is on a logarithmic scale. At an equal mass concentration of HBr is more effective than HCl by a factor 10. For example $10 \text{ mg}/\text{m}^3$ HBr have the same effect as $100 \text{ mg}/\text{m}^3$ of HCl.

In terms of adding ammonium halide upstream of the SCR DeNOx plant to improve mercury co-oxidation of halogen-deficient coals, an economic analysis should be conducted on whether it is more efficient to add NH_4Br rather than NH_4Cl . In the hot flue gases of a high-dust SCR DeNOx plant NH_4Br will be completely dissociated into NH_3 and HBr. At the same time it is as effective as NH_3 or NH_4Cl in promoting the DeNOx reaction (data not shown).

3.2.4. Effect of non-halogen components on Hg^{el} oxidation of DeNOx-inactive SCR catalysts

The effect of the flue gas components O_2 , CO_2 , NO, NO_2 , NH_3 , and SO_2 on the oxidation of elemental Hg was also studied. For this, the H1 catalyst and a model flue gas with $100 \text{ mg}/\text{m}^3$ HCl, 4% by volume (dry) O_2 , 7% by volume H_2O and $40 \mu\text{g}/\text{m}^3$ Hg^{el} were investigated at 390°C by varying the respective components.

It was not possible to detect a measurable influence of 4–21% by volume O_2 in either HCl or in HBr-containing gases. Investigations with CO_2 in the range from 0% to 20% by volume also showed a negligible effect. The addition of $2000 \text{ mg}/\text{m}^3$ SO_2 reduced the mercury oxidation activity of the sample catalyst under the chosen conditions considerably from $20.5 \text{ m}/\text{h}$ to $16.6 \text{ m}/\text{h}$. In HBr-containing gases the effect of SO_2 was smaller.

NO in the gas caused an increase of Hg oxidation as can be seen from Fig. 6. NO_2 had an even stronger effect. For example, in a gas with an inlet concentration of 380 ppm NO and 20 ppm NO_2 the oxidation was increased considerably from $20.5 \text{ m}/\text{h}$ in a gas with no nitrogen oxides to $33.0 \text{ m}/\text{h}$. In the absence of ammonia the SCR DeNOx catalysts will oxidise the influent NO somewhat (DeNOx-inactive status). In this respect, the observed promotional effect

of NO on Hg oxidation during the investigations is likely to be a combined effect of the NO and the NO_2 . It has to be noted, that in a DeNOx active status the promotional effect of NO_2 will not be effective since NO_2 is removed in a fast DeNOx reaction [25].

NH_3 at a concentration of 400 ppm (in the absence of NO) decreased the mercury oxidation activity from $20.5 \text{ m}/\text{h}$ to $14.6 \text{ m}/\text{h}$ respectively. This inhibiting effect of ammonia on the oxidation of elemental mercury has previously been described in literature and is attributed to competitive adsorption of NH_3 with HCl and/or Hg^{el} [16,17].

3.2.5. Reduction of oxidised Hg^{ox} by DeNOx-inactive SCR catalysts

It was recently reported that an SCR catalyst may reduce oxidised Hg in the presence of ammonia [19]. In order to investigate this effect in more detail, model gases under standard conditions (see Section 2) exclusively containing oxidised mercury in the form of HgCl_2 were contacted with the DeNOx-inactive catalyst H1 and the development of Hg was measured at the inlet and the outlet of the catalysts. In flue gases with an HCl or HBr content high enough to prevent adsorption (see Section 3.1), no measurable effects were observed for O_2 , CO_2 , NO and SO_2 in the concentration range to be expected in coal-derived flue gases. The mercury remained fully oxidised downstream of the catalyst. However, 400 ppm NH_3 in the absence of NO gave rise to a measurable reduction of the oxidised Hg. At an

- AV of $19.7 \text{ m}/\text{h}$ 10% and at an
- AV of $11.6 \text{ m}/\text{h}$ 23% of the total mercury appeared as elemental mercury in the effluent gases downstream of the catalyst.

These results showed that adsorbed and activated ammonia in SCR catalysts can reduce Hg^{ox} to a certain degree. In this respect, it was possible to confirm the results of [19]. Thus it can therefore be concluded that the presence of ammonia in the gas did not only

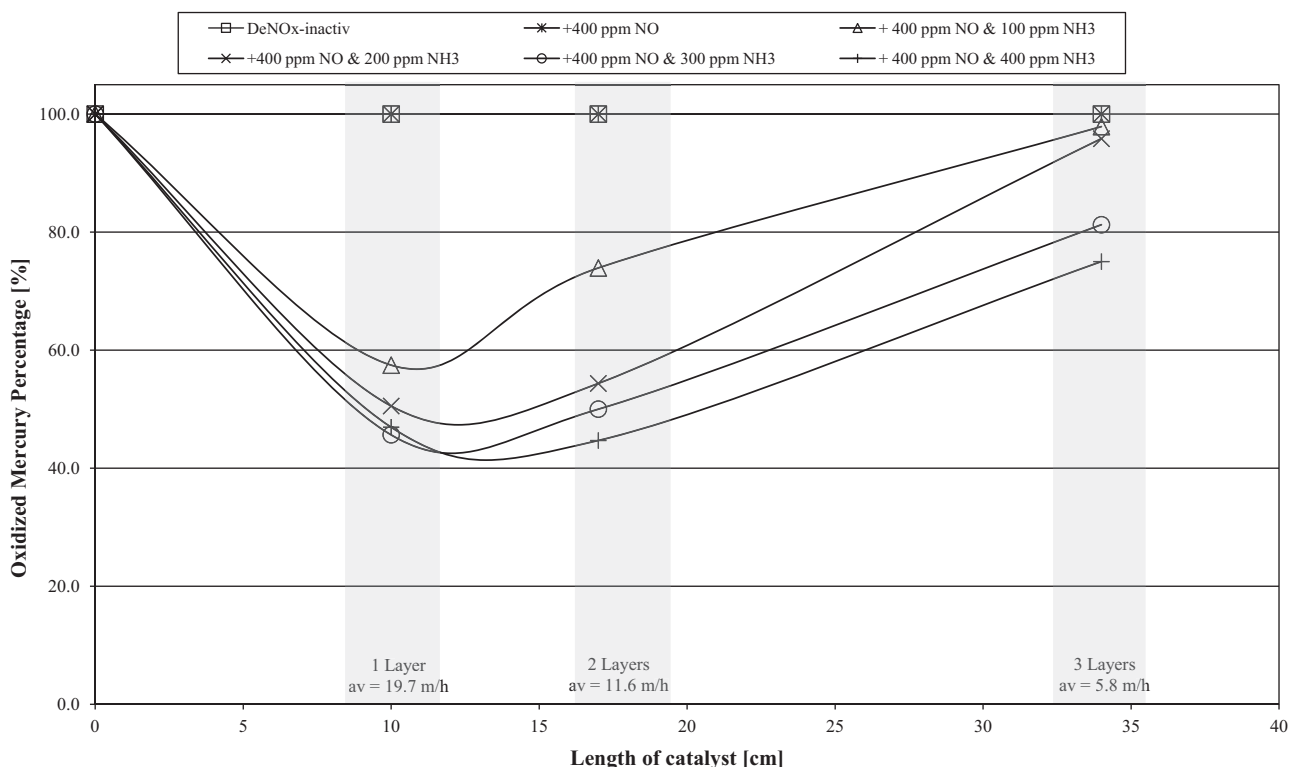


Fig. 7. Percentage of oxidised mercury downstream of the DeNOx-inactive (no NH_3 and NO) and DeNOx-active (with different NH_3/NO ratios) catalyst H1 as function of catalyst length/area velocity AV (influent model flue gas with $40 \mu\text{g}/\text{m}^3$ oxidised mercury, $100 \text{ mg}/\text{m}^3$ HCl, 4% by volume (dry) O_2 , 7% by volume H_2O , 390°C).

inhibit the oxidation of elemental mercury (see Section 3.2.4) but also caused a reduction even in the oxidised mercury.

3.3. Mercury oxidation and induced reduction by DeNOx-active SCR catalysts

With the H1 catalyst, further investigations in the presence of NO and NH_3 , DeNOx-active catalysts, were conducted. Again, the standard model gas with $40 \mu\text{g}/\text{m}^3$ elemental mercury, 4% by volume O_2 , 7% by volume H_2O and $100 \text{ mg}/\text{m}^3$ HCl was used, now with 400 ppm NO, to which NH_3 from 100 ppm up to 400 ppm was simultaneously added.

The percentages of oxidised mercury in the total mercury measured upstream of the first catalyst layer, upstream of the second layer (with an area velocity AV of $19.8 \text{ m}/\text{h}$), upstream of the third layer (AV of $11.6 \text{ m}/\text{h}$) and downstream of the third layer (AV of $5.8 \text{ m}/\text{h}$) for different NH_3/NO ratios are given in Fig. 6. In front of the first catalyst layer, the flue gas contains no oxidised mercury in all flue gases investigated. In the case of the NO and NH_3 -free gas (DeNOx-inactive catalyst), the greatest increase in mercury oxidation occurred in the first layer. The percentage of oxidised mercury was 65.0% behind the first layer, about 78% behind the second and reached complete oxidation behind the third layer respectively. The same gas with the addition of 400 ppm NO caused an even more pronounced increase in oxidation in the first catalyst layer.

The simultaneous presence of 400 ppm NO and 100 ppm ammonia led to a drastic decrease in mercury oxidation in the first catalyst layer to 39%. This effect was enhanced by increasing the ammonia concentration. With 400 ppm NH_3 in the flue gas behind the first catalyst layer, only 31% of the mercury was oxidised. The high NH_3 concentration in the gas and the DeNOx reaction in the catalyst layer have a strong influence on mercury oxidation. Similar effects were observed for the percentage of oxidised mercury over two catalyst layers. The percentage of oxidation drops to 30%. In

DeNOx-active cases, the degree of oxidation increases considerably after the third layer. The third layer provides here the biggest increase in the percentage of oxidised mercury. However, the three layers of the H1 catalyst could no longer ensure complete oxidation of the mercury in the DeNOx-active state. The measured percentage of oxidation was between 77% and 90%. A distinctive negative influence of ammonia and the DeNOx reaction is visible.

The effect of the DeNOx-active catalyst on oxidised mercury was also examined in a series of experiments similar to the one with elemental mercury. The results are illustrated in Fig. 7. As expected, the DeNOx-inactive catalyst did not affect the oxidised mercury across the three catalyst layers, but in the cases where nitrogen oxide and ammonia are present in the influent flue gas a significant formation of elemental mercury across the catalyst was observed. The observed mercury reduction in the presence of NO was much larger than the single effect of NH_3 . 400 ppm ammonia in the absence of NO in the flue gas led to a reduction of the oxidation ratio to 90%. For the DeNOx active case, just 100 ppm NH_3 led to a decreased oxidation ratio of 57% behind the first catalyst layer. The biggest effect occurred in the first layer. In a gas with 400 ppm NO and 400 ppm NH_3 , just 46% of the mercury was oxidised behind the first layer of the catalyst. After the second layer, the percentage of oxidised Hg had already increased in each case investigated. A further sharp increase was observed for the third layer. With 400 ppm NH_3 and NO in the influent flue gas downstream of the third layer, 75% oxidised mercury was measured. The highest mercury reduction took place in the first layer with a high removal of nitrogen oxide. With the decreased DeNOx reaction in the second and especially the third layer, the oxidation potential of the SCR-DeNOx catalyst predominated and led to an increase in the percentage of Hg^{ox} .

A more detailed evaluation of the measured decrease of the NO concentration correlated also with the intensity of the reduction of the influent oxidised mercury (data not given).

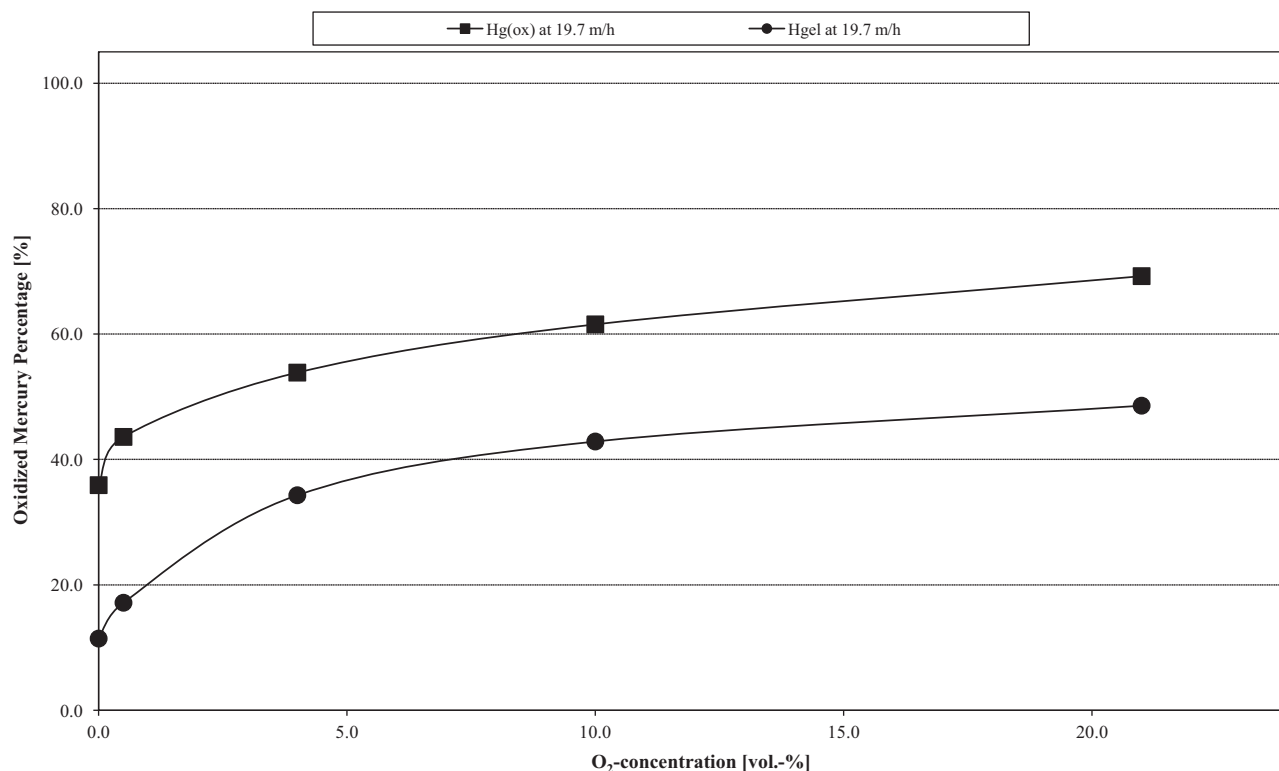
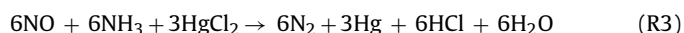


Fig. 8. Effect of the oxygen in the flue gas on the oxidised mercury downstream of the DeNOx-active SCR DeNOx catalyst H1 (influent model flue gas with 40 µg/m³ elemental or oxidised mercury and 100 mg/m³ HCl, 7% by volume H₂O, NO and NH₃ = 400 ppm, AV 19.7 m/h, 390 °C).

Summarising the results it can be said that the effect of ammonia on mercury oxidation is much stronger in the presence of NO and the accompanying DeNOx reactions than in the absence of NO. Without the DeNOx reaction, ammonia decreases the oxidation of elemental mercury. In addition to this effect, the DeNOx reaction is also causing an induced reduction of oxidised mercury. Interestingly, for the investigated catalyst sample H1 and an influent gas with 400 ppm of NO and NH₃ in Figs. 6 and 7, the percentage of mercury oxidation downstream of the three catalyst layers is almost identical and independent of the mercury species upstream of the reactor. Regardless of whether elemental or oxidised mercury is entering, the effect of competitive reduction and oxidation reactions on the catalyst means that equal mercury oxidation was achieved at the outlet of the reactor.

In a hypothesis it will be assumed that the reduction of the oxidised mercury is caused by the intermediate reduced vanadium species produced by the DeNOx reaction in the catalysts. During the DeNOx cycle vanadium will be reduced to V⁴⁺ and V³⁺ and then re-oxidised back to V⁵⁺ by the oxygen in the flue gas [6,26]. The reduced vanadium probably also reacts with other oxidising flue gas components such as the oxidised mercury Hg^{ox} to achieve the original V⁵⁺ state. The sum reaction involving DeNOx and mercury could be formulated as:



In this way, the interaction between the DeNOx reaction and the oxidised mercury may strongly affect the net oxidation of mercury in the SCR DeNOx reactor. The reduction of oxidised mercury caused by intermediates of the nitrogen oxide reduction will hereinafter be referred to as “induced mercury reduction”.

In order to support the hypothesis on the induced reaction in more detail, the influence of the oxygen concentration on the effect of a DeNOx-active catalyst on mercury was studied. In a series of experiments at 390 °C, the model gas with 400 ppm NO and

400 ppm NH₃ and only one catalyst layer H1 the influence of oxygen was investigated over periods of 2 h. The flue gas contained either elemental or oxidised mercury. The oxygen concentration varied from 0% to 21% by volume.

The results are summarised in Fig. 8. Here the measured degree of oxidation of the mercury downstream of the DeNOx active catalysts is given for two borderline cases, influent flue gases containing either 100% elemental or oxidised mercury. For the influent gas with elemental mercury the degree of oxidation downstream of the catalyst as shown in Fig. 8 represents an oxidation, whereas for the oxidised mercury a degree of oxidation below 100% shows a reduction of mercury by the catalyst.

From Fig. 8 it can be seen that for the oxygen-free flue gas, 11.4% of the influent elemental mercury was oxidised and 35.9% of the incoming oxidised mercury remained oxidised when passing the DeNOx-active catalyst, while a flue gas containing 21% of oxygen showed an oxidation ratio of 49% for elemental mercury and 69% for the oxidised mercury. Obviously the induced reductive effect of the DeNOx reaction on mercury was decreased by oxygen in the flue gas but was not completely suppressed. Similar experiments with the DeNOx-inactive catalyst resulted in a non-detectable influence of the oxygen on the mercury reaction (see Section 3.2.4).

3.4. Induced mercury reduction on VOC-active catalysts

SCR DeNOx catalysts are also used to control the emission of dioxins and volatile organic compounds (VOC) in flue gases from hazardous waste incineration plants [7]. In this way, the organic compounds are frequently oxidatively degraded with CO as an important end product. During the oxidation of VOC on DeNOx catalysts, reduced vanadium species are formed [27,28]. The re-oxidation of this vanadium is usually achieved by oxygen in the exhaust gas to be treated, analogous with the reaction that closes the reduction-oxidation cycle of the DeNOx reaction. It was

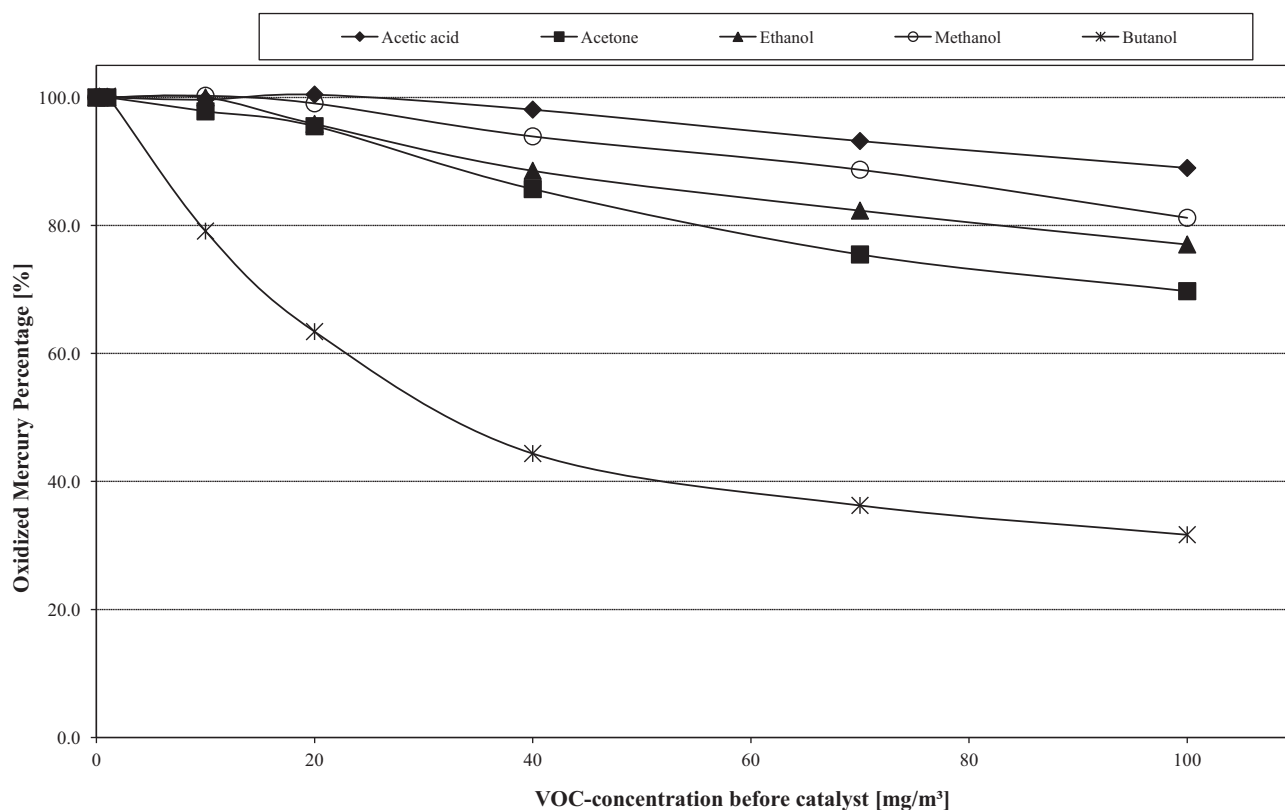


Fig. 9. Effect of the influent VOC concentration on the oxidised mercury downstream of the DeNOx inactive SCR DeNOx catalyst H1 (influent model flue gas with 40 $\mu\text{g}/\text{m}^3$ oxidised mercury, 100 mg/m^3 HCl, 4% by volume (dry) O_2 , 7% by volume H_2O , AV 19.7 m/h, 390 °C).

interesting to see whether Hg^{ox} could also interact with the reduced vanadium intermediately formed by the reaction with VOCs.

For this, HgCl_2 -containing model flue gases with a high VOC content were contacted with the H1 DeNOx catalyst (see Table 1). In particular, the VOCs acetic acid, acetone, ethanol, methanol and butanol in concentrations up to 100 mg/m^3 were investigated. The model flue gas contained otherwise 21% by volume O_2 , 7% by volume H_2O , 100 mg/m^3 HCl and no NO or NH_3 . The reaction temperature was set at 390 °C and the area velocity at 19.7 m/s.

The results are summarised in Fig. 9. The entering Hg^{ox} was reduced by the VOC-active DeNOx catalysts. The degree of reduction increased with increasing concentration of the VOC in the gas. On the same basis of mass concentration, the reduction of the oxidised mercury followed the order:

acetic acid < methanol < ethanol < acetone \ll butanol

Obviously, the more oxidised the VOC the smaller its effect on the oxidised mercury. Butanol was the most effective VOC investigated. 30 mg/m^3 butanol in the model gas was sufficient to reduce 50% of the entering Hg^{ox} . Under the chosen conditions, the reduction of mercury was considerably faster than the oxidation of the Hg^{el} produced.

A more detailed evaluation of the measured decrease of the VOC concentration correlated with the reduction of the influent oxidised mercury (data not given). The VOC were partially oxidised to carbon monoxide CO. In the comparison the correlation between the measured increase of the CO concentration and the reduction of mercury proven to be less pronounced.

The results in Fig. 9 support the hypothesis that the reduced vanadium species formed intermediately on the DeNOx catalysts does have a reducing effect on oxidised mercury in flue gases. It is proposed that this effect be called induced reduction of Hg^{ox} on DeNOx catalysts. The induced reduction will have to include

more refined models of catalytic mercury oxidation on vanadium containing catalysts in future. In principle, the induced reduction concept implies that all of the oxidation reactions that take place on the catalyst will have a negative effect on the net oxidation of Hg^{el} , see also Fig. 10.

4. Summary and conclusion

For the effective co-removal in scrubbers, the mercury in flue gases has to be in an oxidised form. The present investigation aims to improve catalytic processes for increasing the percentage of oxidised mercury in flue gases. In a series of model investigations under defined conditions, the influence of gas-related and catalyst-related parameters on the co-oxidation of mercury in high-dust SCR DeNOx reactors upstream of scrubbers was clarified.

A primary requisite for mercury oxidation on commercial DeNOx catalysts is the presence of halogen halides in the flue gas. The oxidation rate will increase with increasing halogen halide content in the gas to be treated. Hydrogen bromide on a mass basis proved to be around ten times more effective than hydrogen chloride in this respect. The bromine content of the fuel incinerated will determine the hydrogen bromide content in the resulting flue gas and consequently may be a decisive factor in the oxidation of mercury in a DeNOx plant.

Another important parameter for the mercury oxidation activity is the vanadium content of the catalyst.

For the DeNOx-inactive catalysts and a given constant halogen halide concentration in the flue gas, the rate of oxidation of the mercury can be modelled as a first order reaction of the Hg^{el} concentration. For the twelve commercial SCR DeNOx catalysts examined the DeNOx activity was between 2 and 0.8 times the mercury oxidation activity. Mercury oxidation is a comparably fast reaction. The carbon dioxide and oxygen content did not affect the oxidation

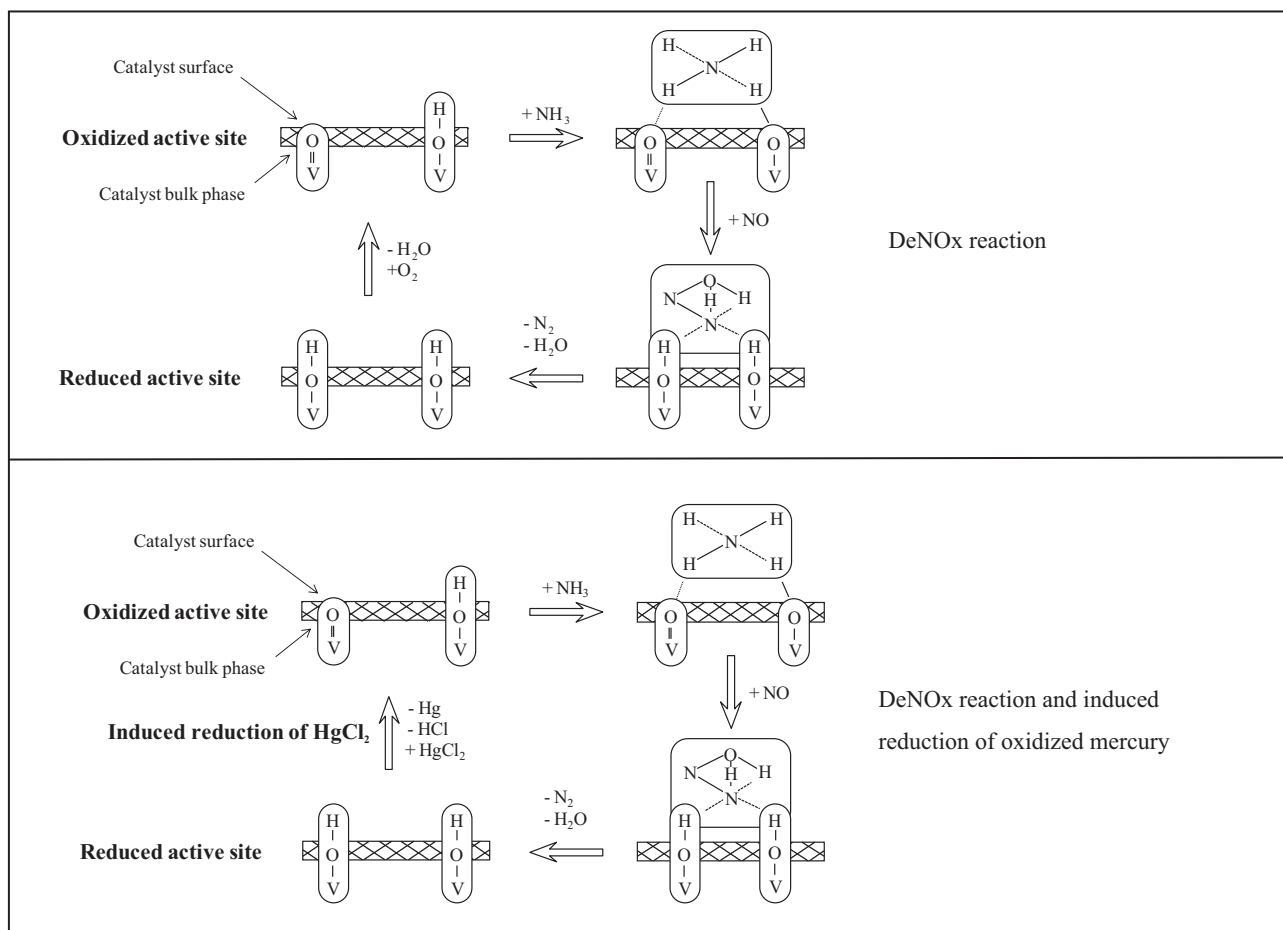


Fig. 10. Schematic mechanism for the induced mercury reduction by the SCR-DeNOx reaction.

of elemental mercury on DeNOx-inactive catalysts observably. The addition of nitrogen oxides (in the absent of ammonia) increased the oxidation of elemental mercury somewhat, whereas SO_2 and ammonia (in the absent of nitrogen oxides) decreased the rate.

Oxidised mercury in the influent gas was not affected by the halogen halide, carbon dioxide and nitrogen oxide content. Influent oxidised mercury was decreased somewhat by ammonia in the flue gas in contact with DeNOx-inactive catalysts, it was possible to measure elemental mercury downstream of the catalyst. Obviously, ammonia is not only inhibiting the oxidation of elemental mercury by blocking active sites of the catalyst, as discussed in the literature, but may also exert a reducing effect on the oxidised mercury.

It was possible to show that DeNOx-active catalysts, and respectively the simultaneous presence of nitrogen oxides, ammonia and DeNOx catalysts, has a strong negative effect on mercury oxidation. Not only is the oxidation of elementary mercury slowed, but influent oxidised mercury is also transformed into the elementary species. With the consumption of the ammonia and nitrogen oxide in the DeNOx reaction along the gas flow through the catalyst, the reductive effect on oxidised mercury decreases and mercury oxidation by the catalysts begins to dominate. On DeNOx-active SCR catalysts two reactions involving mercury compete, the reduction of oxidised mercury by the DeNOx-active catalysts and the well known oxidation of elementary mercury throughout the catalyst. The reducing effect dominates the net reaction of mercury in the inflow section of SCR catalysts, whereas the oxidation dominates in the outflow section. The reducing effect on oxidised mercury was also observed in DeNOx catalysts which oxidised volatile organic compounds (VOC-active catalysts). This effect of SCR DeNOx catalysts is termed induced mercury reduction. It is assumed that

the induced reduction is caused by reduced vanadium species formed intermittently in the DeNOx and VOC-reactions. The induced reduction of mercury was more pronounced in flue gases with low oxygen content, supporting the induced oxidation mechanism.

The present investigation confirms that to achieve a high ratio of oxidised mercury in the flue gas downstream of an SCR DeNOx plant it is necessary to have sufficient DeNOx-inactive and mercury-active catalyst surfaces on the downstream side of the DeNOx reactor. The influent oxidised mercury will be strongly affected by the induced reduction exerted by the DeNOx-active catalyst section of the DeNOx reactor and to a certain extent by the high ammonia concentration in this section. The results indicate that the state of oxidation of the mercury in the influent gas may have only a small effect on its net overall oxidation if the reactor is operated at area velocities of 6 m/h.

The unexpected results of a likely strong interference between the “trace reactions” of the mercury and the major reactions of the NOx and VOC need fundamental research efforts for further clarification.

In the experimental investigation an external mass transfer situation typical for industrial SCR DeNOx plants was simulated. No attempt has been made to study the effects of intraporous mass transfer on the interaction between the DeNOx and the mercury oxidation reaction. For example, the quite different diffusion coefficients of the involved species NO, NH_3 and Hg are likely to effect the interaction of the two reactions due to the role diffusion plays within in the overall kinetics. Further investigations should address this aspect in order to gain a deeper understanding of the kinetics.

Acknowledgments

This work was funded by E.ON Engineering GmbH Gelsenkirchen, a Max Buchner scholarship and a postgraduate scholarship from the Martin-Luther-University Halle-Wittenberg. The authors are grateful to the former graduate students Reinhard Schimpfermann, Marco Kuehn and Mei Tang for their support with laboratory research and to Prof. Bernhard Vosteen for many helpful discussions during the investigations.

References

- [1] UNEP, Mercury fate and transport in the global atmosphere: measurements, models and policy implications, Interim Report of the UNEP Global Mercury Partnership, 2008.
- [2] B. Krishnakumar, S. Niksa, L. Sloss, W. Jozewics, G. Futsaeter, *Energy Fuels* 26 (2012) 4624–4634.
- [3] C.L. Senior, *Journal of the Air & Waste Management Association* 56 (2006) 23–31.
- [4] B. Krishnakumar, J.J. Helble, *Fuel Processing Technology* 94 (2012) 1–9.
- [5] B. Van Otten, P.A. Buitrago, C.L. Senior, G.D. Silcox, *Energy Fuels* 25 (2011) 3530–3536.
- [6] G. Busca, L. Lietti, G. Ramis, F. Berti, *Applied Catalysis B* 18 (1998) 1–36.
- [7] A. Hadzic, *Chemical & Biochemical Engineering* 24 (2010) 401–408.
- [8] C. Richardson, T. Machalek, S. Miller, C. Dene, R. Chang, *Journal of the Air & Waste Management Association* 52 (2002) 941–947.
- [9] H. Gutberlet, A. Spiesberger, F. Kastner, J. Tembrink, *VGB Kraftwerkstechnik* 72 (1992) 636–641.
- [10] A.A. Presto, E.J. Granite, *Environmental Science & Technology* 40 (2006) 5601–5609.
- [11] B.A. Dranga, L. Lazar, H. Koeser, *Catalysts* 2 (2012) 139–170.
- [12] S. Straube, T. Hahn, H. Koeser, *Applied Catalysis B* 79 (2008) 286–295.
- [13] Y. Zhuang, J. Laumb, R. Liggett, M. Holmes, J. Pavlish, *Fuel Processing Technology* 88 (2007) 929–934.
- [14] H.M. Yang, W.P. Pan, *Journal of Environmental Sciences* 19 (2007) 181–184.
- [15] C.W. Lee, S.D. Serre, Y. Zhao, S.J. Lee, T.W. Hastings, *Journal of the Air & Waste Management Association* 58 (2008) 484–493.
- [16] M. Rallo, B. Heidel, K. Brechtel, M.M. Maroto-Valer, *Chemical Engineering Journal* 198–199 (2012) 87–94.
- [17] S. Niksa, N. Fujiwara, *Journal of the Air & Waste Management Association* 55 (2005) 1866–1875.
- [18] S. Niksa, A.F. Sibley, *Industrial & Engineering Chemistry Research* 49 (2010) 6332–6341.
- [19] K. Madsen, D.A. Jensen, J.F. Frandsen, R.J. Thøgersen, A mechanistic study on the inhibition of the DeNO_x reaction on the mercury oxidation over SCR catalysts, in: *Proceedings of Air Quality VIII Conference*, Arlington, October 24–27, 2011.
- [20] H. Gutberlet, J. Tembrink, Dry sampling method used by E.ON for mercury speciation in flue gases, in: *EPRI Workshop*, Pittsburgh, PA, July, 2004.
- [21] VGB-Guideline 302 He: Guideline for the Testing of DENOX Catalysts, VGB Technical Association of Large Power Plant Operators, Germany, 1998.
- [22] T. Nagayasu, H. Nakashoji, N. Imai, *VGB Power Tech* 91 (4) (2011) 68–73.
- [23] B.W. Vosteen, H. Winkler, M.S. Berry, Native halogens in coals from US, China, and elsewhere – low chlorine coals need bromide addition for enhanced mercury capture, in: *A&WMAs Power Plant Air Pollutant Control MEGA Symposium*, Baltimore, 2010.
- [24] B.W. Vosteen, R. Kanefke, H. Koeser, *VGB Power Tech* 86 (3) (2006) 70–75.
- [25] E. Tronconi, I. Nova, C. Ciardelli, D. Chatterjee, M. Weibel, *Journal of Catalysis* 245 (2007) 1–10.
- [26] N.-Y. Topsoe, J.A. Dumesic, H. Topsoe, *Journal of Catalysis* 151 (1995) 241–252.
- [27] P. Mars, D.W. van Krevelen, *Chemical Engineering Science* 3 (Suppl. 1) (1954) 41–59.
- [28] M. Witko, K. Hermann, R. Tokarz, *Catalysis Today* 50 (1999) 553–565.